Synthesis of Optically Pure Bisphosphine Oxides and Related Compounds

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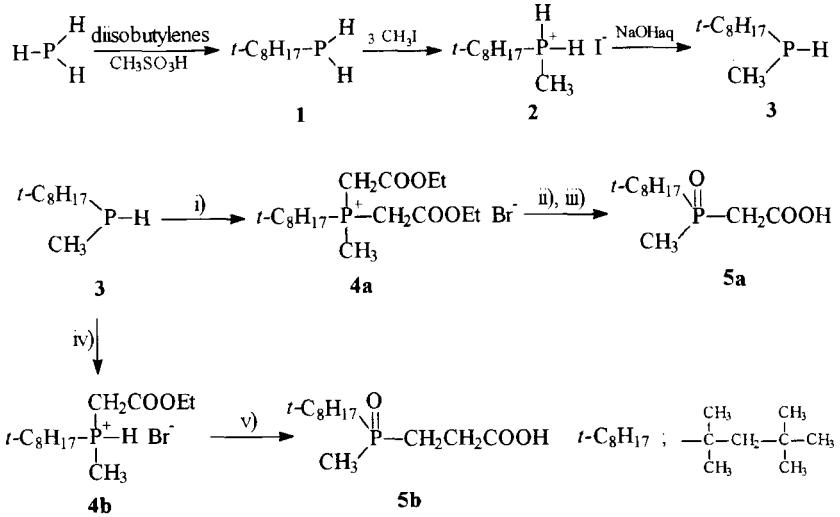
Optically pure bisphosphine oxides were conveniently synthesized by Kolbe electrolytic coupling reaction of carboxylic acids possessing a chiral phosphinoyl group in 60—65% isolated yield. This synthetic approach provides a variety of accesses to P-chiral bisphosphine ligands. Their absolute configurations were intercorrelated with that of the previous reported BisP*–borane. Asymmetric hydrogenation of α-(acylamino)acrylic acids by a rhodium complex with BisP* (R = *t*-octyl or 1,1,3,3-tetramethylbutyl) affords *N*-acylamino acids in 94—96% ee.

Some chiral phosphine compounds have been used as ligands in a wide variety of metal-catalyzed asymmetric reactions.[1] Recently, Imamoto et al. developed the P-chiral bisphosphine ligands (BisP*),[2] 1,2-bis(alkylmethylphosphino)ethanes, which have two phosphorus atoms bearing one bulky alkyl group and one methyl group. They have shown that their Rh-complex catalysts have high enantioselectivity in asymmetric hydrogenation reactions. The method employed by Imamoto et al. for the construction of C_2-symmetric bisphosphines implies copper-promoted oxidative coupling of chiral phosphine–boranes (1/2).

In a preliminary letter, we reported a method for producing bisphosphine oxides by Kolbe electrolytic coupling reaction of phosphinoyl carboxylic acids.[3] We expected that the Kolbe coupling products should keep the configurations as asymmetric carbon did.[4] Furthermore, it is possible to obtain the bisphosphine oxides in which a polymethylene group longer than ethylene bridges between phosphorus atoms. We now report a new approach to BisP* and related bisphosphines based on the electrochemical Kolbe coupling of chiral phosphinoyl carboxylic acids. In addition, we describe the results of asymmetric hydrogenation of α-(acylamino)acrylic acids by a rhodium complex with BisP* having a new bulky alkyl group (*t*-octyl or 1,1,3,3-tetramethylbutyl).

Results and Discussion

Synthesis and Resolution. Methyl(1,1,3,3-tetramethylbutyl)phosphine (**3**) was synthesized in two steps from phosphine (PH_3) in 56.2% overall yield (Scheme 1). At the first step, the acid-catalyzed addition of phosphine to "diiso-



Scheme 1. Preparation of phosphinoyl carboxylic acids (**5a** and **5b**). i) $BrCH_2COOEt$, ii) NaOHaq, iii) HClaq, iv) CH_2=CHCOOH, v) H_2O_2aq.

butylenes" (a mixture of 2,4,4-trimethyl-1- and -2-pentenes) gave (1,1,3,3-tetramethylbutyl)phosphine (**1**), which was reacted with excess iodomethane to form the corresponding phosphonium salt **2**. The salt was decomposed under basic conditions to give **3**. Racemic phosphinoyl carboxylic acid derivatives **5a** and **5b** were obtained starting from **3** in good yields. Treatment of **3** with ethyl bromoacetate resulted in the formation of phosphonium salt **4a**. The formed salt **4a** on treatment with aqueous NaOH solution salt was quantitatively oxidized by air to form compound **5a**. Addition reaction of the secondary phosphine to acrylic acid was carried out in the presence of concentrated hydrochloric acid. The formed salt **4b** was quantitatively oxidized by hydrogen peroxide to form compound **5b**.

Figure 1 shows typical resolution of racemic **5a** by the fractional crystallization using (−)-(*S*)-1-phenylethylamine (PEA) as a resolving agent. Optically pure (−)-**5a** was obtained by thrice-repeated recrystallization from ethyl methyl ketone or acetone. The filtrate was allowed to stand overnight at room temperature; subsequent further fractional crystallization gave optically pure (+)-**5a**.

Optically pure (+)- and (−)-**5b** were obtained by using optically active PEA as a resolving agent in a similar manner. Stereochemistry will be described below.

Kolbe Electrolytic Coupling Reaction. Kolbe electrolytic coupling reactions of chiral phosphinoyl carboxylic acids were carried out in methanol with a small amount of CH_3ONa as a supporting electrolyte using platinum electrodes at a constant current density of 87.5 mA cm^{-2}, applied voltage ca. 28 V, at 10—20 °C for 2 h to give P-chiral bisphosphine oxides in 60—65% isolated yield (Scheme 2).

Electrolysis of racemic **5b** afforded 35.2% of *meso*-bisphosphine oxide (*meso*-**6b**), 27.1% of *dl*-bisphosphine oxide (*dl*-**6b**), 9.3% of methyl ester **9b**, 9.1% of methyl ether **10b**, 3.7% of vinylphosphine oxide **11**, and ethylmethyl(1,1,3,3-tetramethylbutyl)phosphine oxide (**12**) (Scheme 3). The products were isolated and identified by ^{1}H NMR, ^{31}P NMR, FAB-Mass, and FT-IR specrtroscopies. Methyl ester **9b** is

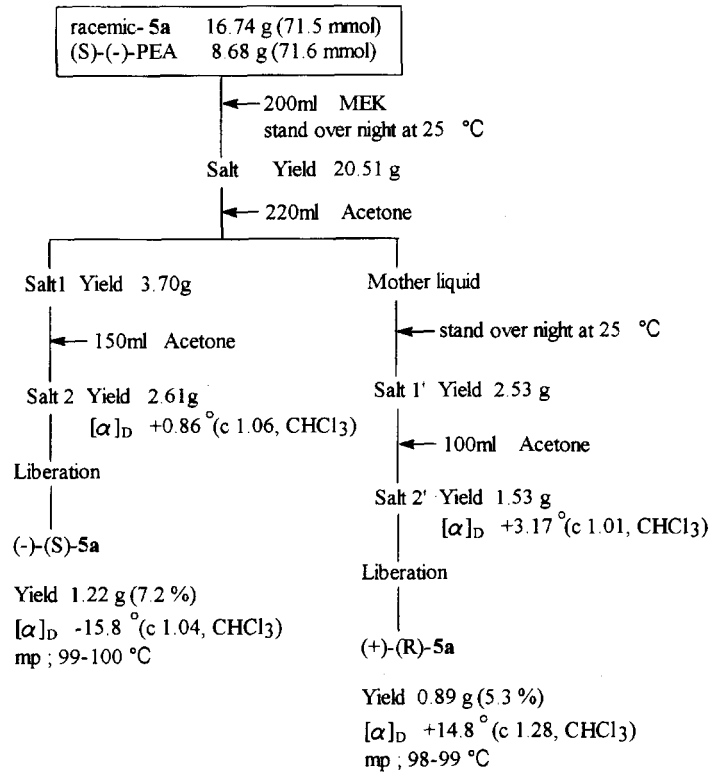
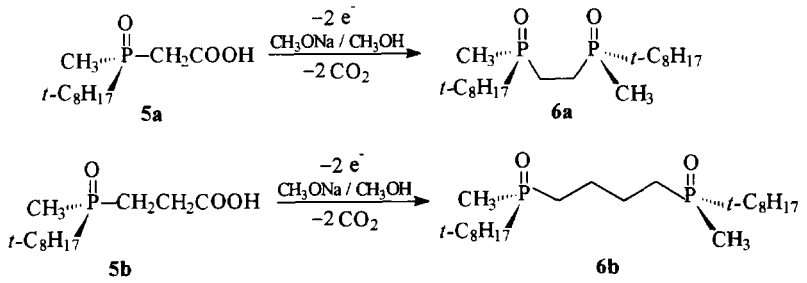
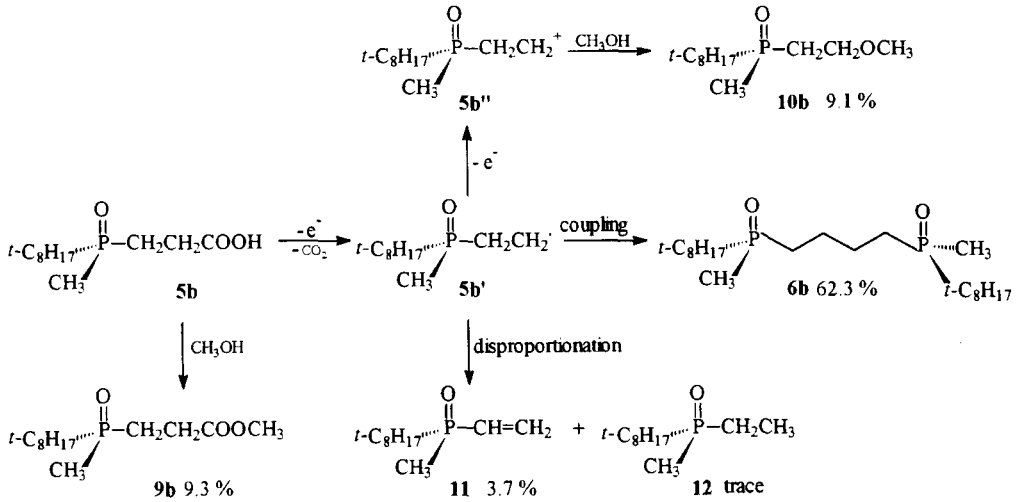


Fig. 1. Optical resolution of racemic-**5a** using (−)-PEA as a resolving agent.



Scheme 2. The Kolbe electrolytic coupling reactions.



Scheme 3. The side reactions of Kolbe electrolysis of **5b**.

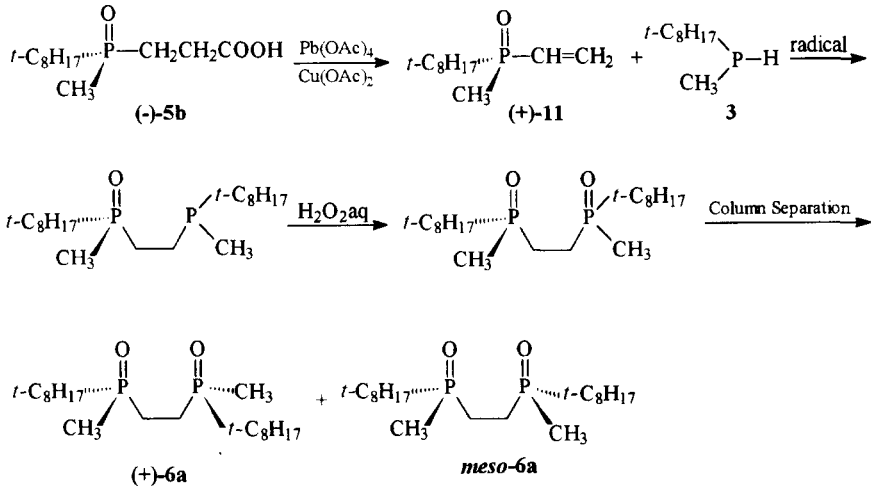
apparently formed by esterification of **5b**. Alkyl radical (**5b′**) undergoes disproportionation to yield **11** and **12**. Methyl ether **10b** may be formed by methanolysis of **1b″** produced by oxidation of **1b′**.

Preparation of 6a by Free-Radical Addition. Decarboxylation of (−)-**5b**, $[\alpha]_D^{20}$ −10.79°, by Pb (IV) acetate gave (+)-**11**, $[\alpha]_D^{24}$ +29.15°, in 32.6% overall yield (Scheme 4). Free-radical addition of secondary phosphine to (+)-**11** was initiated by organic peroxides. The following oxidation with hydrogen peroxide afforded **6a**. Optically pure (+)-**6a**, $[\alpha]_D^{20}$ +2.80° and *meso*-**6a** were separated by column chromatography. This synthetic approach provides accesses to a variety of bisphosphine oxides.

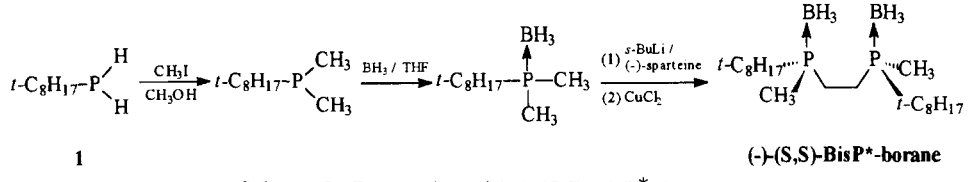
Stereochemistry. Bisphosphine–borane (1/2) (−)-**8a**, $[\alpha]_D^{20}$ −5.56°, was synthesized by reduction of (+)-**6a** with $PhSiH_3$,[8] followed by reaction with THF–borane (1/1)[9] with complete retention of configuration at phosphorus atom in 62% overall yield. Racemization of bisphosphine **7a** occurred to an extent of 11.3% determined by ^{31}P NMR spectrum.

The *S,S*-configuration of several BisP*–boranes prepared by Imamoto et al. have been confirmed by X-ray analysis.[2] We synthesized the BisP*–borane having *t*-octyl group according to this manner, and deduced that it had the same *S,S*-configuration (Scheme 5).

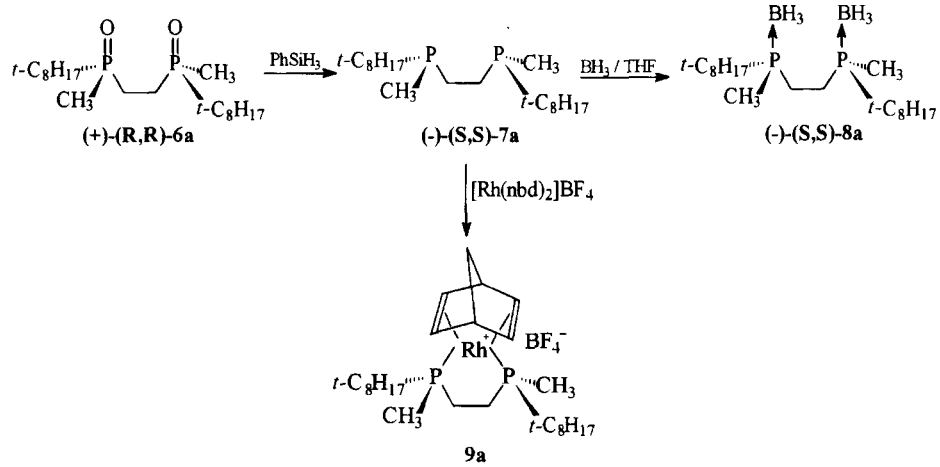
The value of optical rotation of this sample, $[\alpha]_D^{20}$ −5.68°, was in very close agreement with that of bisphosphine–borane **8a**, $[\alpha]_D^{20}$ −5.56°, prepared via Kolbe oxidation. There-



Scheme 4. Preparation of chiral **6a** via radical addition of vinylphosphine oxide **11** to secondary phosphine **3**.



Scheme 5. Preparation of (−)-(*S,S*)-BisP*–borane.



Scheme 6. Absolute configurations, and the preparation of Rh-complex **9a**.

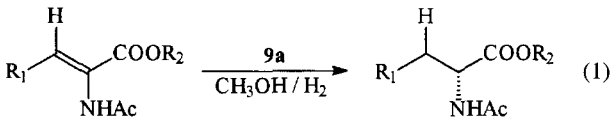


Table 1. Rh-Catalyzed Enantioselective Hydrogenation of α-(Acylamino)acrylic Derivertives (Eq. 1)

Entry	R_1	R_2	Temp (°C)	Time (min)	S/C	H_2 (atm)	% ee (config.)[a]
1	H	CH_3	R.T.	300	1000	2	94.5[c] (*R*)
2	H	CH_3	R.T.	70	500	2	96.3[c] (*R*)
3	H	CH_3	R.T.	60	500	6	75.6[c] (*R*)
4	H	CH_3	5—10	60	500	2	81.8[b,c] (*R*)
5	H	CH_3	50	10	500	2	93.2[c] (*R*)
6	Ph	H	R.T.	120	500	2	93.5[d] (*R*)
7	Ph	H	R.T.	90	500	6	89.7[d] (*R*)

a) Absolute configuration were confirmed by comparison of chiral GC or HPLC elution order. b) Chemical yield; 37.9%. c) The ee (%) values were determined by chiral capillary GC using Chrompack's Chiral-L-Val (25 m). d) The ee (%) values were determined by HPLC using a Daicel Chiral OD-H column.

fore, we conclude that our method also gives (−)-(*S*,*S*)-bisphosphines. In addition, (−)-(*S*,*S*)-**7a** was converted to the cationic rhodium complex **9a** by the reaction with [Rh-(nbd)]$_2$BF$_4$ (Scheme 6).

Asymmetric Hydrogenation. The rhodium complex **9a** was employed as the catalyst in asymmetric hydrogenation of α-(acylamino)acrylic derivatives. Runs **2** and **6** were carried out at room temperature and an initial hydrogen pressure of 2 atm in the presence of the catalyst (0.2 mol%). Reactions proceeded rapidly and were completed within 1—2 h, and provided high enantioselectivities as 94—96% ee. Runs 3 and 7 were carried out at an initial pressure of 6 atm: The general trend is: The higher the pressure, the lower the optical yields. These results are summarized in Table 1.

Experimental

IR spectra were determined with a JASCO FT/IR-430 spectrometer. NMR spectra were obtained on a JEOL JNM-LA300 spectrometer (300 MHz ^{1}H, 121.6 MHz ^{31}P, 75.5 MHz ^{13}C). ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ using TMS as an internal standard. ^{31}P NMR spectra were taken by using 85% H_3PO_4 as an external standard. GC-Mass spectra were obtained on a JEOL JMS-DX303 with 70 eV ionization potential and the molecular ions were cited: *m*/*z*. FAB-Mass spectra were obtained on a JEOL JMS-DX303. Elemental analysis was performed on a Perkin–Elmer Model 2400II elemental analyzer. Optical rotations were measured on a Horiba SEPA-300 Polarimeter, using the 589.3 nm D-line of sodium. HPLC analysis was performed using a Hitachi L-7000 series interfaced to a LaChrom computer workstation. Melting points were measured on a Yanaco MP-500V with a hot stage microscope, and were uncorrected. Air-sensitive reactions were performed using usual inert atmosphere techniques.

Electrolysis Apparatus. The electrolytic vessel was a tall-form beaker, diam. 3 cm, height 10 cm, fitted with a gas lead pipe, thermometer and magnetic stirrer, two smooth platinum electrodes (2 cm×4 cm) being placed parallel to each other 1 mm apart. The cell was cooled with an ice water bath. The electrolyse was carried out by the use of a Yamabishi MD 35-3 regulated DC power supply.

Preparation of Methyl(1,1,3,3-tetramethylbutyl)phosphine (3).[8] In a 500 ml four-neck flask, (1,1,3,3-tetramethylbutyl)-phosphine **1**[9] (105.7 g, 0.75 mol) and iodomethane (319.4 g, 2.25

mol) were reacted at room temperature and then stirred for 6 h under nitrogen. The reaction mixture became a yellowish-white solid. The excess amount of iodomethane was removed by under reduced pressure. The resulting residue **2** was dissolved in 300 ml of 5 M NaOH solution (1 M = 1 mol dm^{-3}) under nitrogen atmosphere, and extracted by 300 ml of hexane. The extract was washed with water, dried (Na_2SO_4), and concentrated. Distillation of the residual oil under reduced pressure gave 101.4 g (84.4%) of a colorless liquid **3**: Bp 63—66 °C/16 mmHg (1 mmHg = 133.322 Pa); ^{1}H NMR ($CDCl_3$) δ = 0.99 (s, 9H), 1.01 (d, 3H, ^2J = 3.13 Hz), 1.20 (d, 6H, ^3J = 11.82 Hz), 1.42 (d, 2H, ^3J = 9.2 Hz), 3.00 (d, 1H, ^1J = 181.1 Hz); ^{13}C NMR ($CDCl_3$) δ = 0.76 (d, ^1J = 17.1 Hz), 28.84 (d, ^2J = 8.5 Hz), 30.74 (d, ^4J = 8.6 Hz), 31.90 (d, ^1J = 3.0 Hz), 33.12 (d, ^3J = 6.7 Hz), 53.83 (d, ^2J = 14.0 Hz); ^{31}P NMR ($CDCl_3$) δ = −33.80 (d, ^1J = 181.1 Hz); FT-IR (neat) 2965, 2280, 1470, 1364, 1296, 1236, 972 cm^{-1}; GC-MS (*m/z*) 160 (M^+).

Preparation of [Methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]acetic Acid (5a).[10] A solution of **3** (48.0 g, 0.30 mol) and ethyl bromoacetate (103.5 g, 0.62 mol) in 150 ml of ethyl alcohol was heated at ca. 80 °C for 3 h with stirring under nitrogen. The solvent was removed under reduced pressure and the residue **4a** was dissolved in 200 ml of water. Then 130 ml of 5 M NaOH solution was added dropwise while the temperature was kept at 80—90 °C. After completion of the dropping, the mixture was kept at 90 °C for 2 h. After being cooled to room temperature the mixture was acidified with concentrated hydrochloric acid. The acidic solution was extracted with 300 ml of chloroform twice. The combined extract was washed with water, dried (Na_2SO_4), and concentrated. Recrystallization of the residual oil from acetone gave 17.1 g (24.4%) of a white crystal of **5a**: Mp 127—129 °C; ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 9H), 1.34 (d, 6H, ^3J = 17.9 Hz), 1.52 (d, 2H, ^3J = 8.8 Hz), 1.71 (d, 3H, ^2J = 12.3 Hz), 2.71 (dd, 1H, ^2J = 9.2 Hz, J_{gem} = 13.4 Hz), 3.00 (dd, 1H, ^2J = 14.3 Hz, J_{gem} = 13.4 Hz), 10.78 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 9.26 (d, ^1J = 64.6 Hz), 21.09 (s), 32.05 (s), 32.99 (d, ^1J = 34.1 Hz), 33.41 (s), 36.9 (d, ^1J = 67.0 Hz), 45.49 (s), 168.71 (d, ^2J = 6.1 Hz); ^{31}P NMR ($CDCl_3$) δ = 59.56 (s); FT-IR (KBr) 2955, 1715, 1269, 1158, 1103, 897 cm^{-1}; FAB-MS (Pos., *m/z*) 235 $[M+H]^+$. Anal. Calcd for $C_{11}H_{23}O_3P$: C, 56.40; H, 9.90%. Found: C, 56.45; H, 10.04%.

Preparation of 3-[Methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]propionic Acid (5b).[11] In a 500 ml flask, **3** (80.0 g, 0.50 mol) and 35% concentrated hydrochloric acid (156.0 g, 1.5 mol) were charged therein under nitrogen. Acrylic acid (36.0 g, 0.5 mol) was added dropwise with stirring while the temperature was kept at 30 °C or less. The reaction mixture became a homogeneous, colorless, and transparent liquid. The liquid was concentrated under reduced pressure and the excess amounts of hydrochloric acid and water were removed. The resulting mixture **4b** was dissolved in 200 ml of water; 55.0 g (0.55 mol) 34% hydrogen peroxide was added dropwise while the temperature was kept at 60—70 °C. After completion of the dropping, the mixture was matured at 90 °C for 1 h. The solvent was removed under reduced pressure and the residue was extracted with 300 ml of chloroform twice. The combined extract was washed with water, dried (Na_2SO_4), and concentrated. Recrystallization of the residual oil from acetone gave 79.0 g (63.7%) of a white crystal of **5b**: Mp 100—103 °C; ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 9H), 1.35 (d, 6H, ^3J = 17.6 Hz), 1.50 (d, 2H, ^3J = 8.6 Hz), 1.59 (d, 3H, ^2J = 11.7 Hz), 2.09—2.18 (m, 1H), 2.20—2.38 (m, 1H), 2.57—2.80 (m, 2H), 11.81 (s, 1H); ^{13}C NMR ($CDCl_3$) δ = 7.97 (d, ^1J = 61.5 Hz), 18.40 (d, ^1J = 62.7 Hz), 20.87 (d, ^2J = 4.8 Hz), 26.68 (d, ^2J = 3.7 Hz), 31.92 (s), 33.23 (d, ^2J = 14.6 Hz), 36.14 (d, ^1J = 64.0 Hz), 45.27 (s), 173.75 (d, ^3J = 10.9 Hz); ^{31}P NMR ($CDCl_3$) δ = 61.99 (s); FT-IR (KBr) 2963, 1736, 1421, 1233, 1174, 902 cm^{-1}; FAB-MS (Pos., *m/z*) 249 $[M+H]^+$. Anal. Calcd for $C_{12}H_{25}O_3P$: C, 58.05; H, 10.15%. Found: C, 58.45; H, 10.90%.

Optical Resolution of 5a. (−)-(*S*)-1-Phenylethylamine (8.68 g, 71.6 mmol) was added to a solution of **5a** (16.74 g, 71.5 mmol) in 200 ml of ethyl methyl ketone. The solution was allowed to stand overnight at room temperature. The salt which precipitated was collected by filteration (yield 20.51 g; Mp 121—123 °C; $[\alpha]_D^{25}$ −1.89° (*c* 1.212, $CHCl_3$)). The salt was recrystallized from 220 ml of acetone at room temperature (yield 3.70 g). Further recrystallization was carried out by using 150 ml of acetone at −15 °C (yield 2.61; Mp 137—138 °C; $[\alpha]_D^{25}$ +0.86° (*c* 1.062, $CHCl_3$)). The salt was liberated by using hydrochloric acid solution and extracted with dichloromethane. The organic solution was dried over Na_2SO_4. Evaporation gave optically pure (−)-**5a** in 1.22 g (7.2%) yield.: Mp 99—100 °C; $[\alpha]_D^{25}$ −15.8° (*c* 1.04, $CHCl_3$); Optical purity (98.6% ee) was determined by HPLC with Daicel Chiralcel OD-RH (CH_3CN : phosphate buffer at pH 2 = 15 : 85); flow rate 0.2 ml min^{-1}; UV detector 215 nm; temperature 30 °C; retention time; 25.7 min for (−)-**1a**, 27.8 min for (+)-**5a**.

The mother liquid of (+)-rich **5a** salt was allowed to stand overnight at room temperature and subsequent further fractional crystallization was carried out (yield 1.53 g; mp 129—131 °C; $[\alpha]_D^{22}$ +3.17° (*c* 1.008, $CHCl_3$)). Subsequent liberation of the acid, extraction, and evaporation gave optically pure (+)-**5a** in 0.89 g (5.3%) yield.: Mp 98—99 °C; $[\alpha]_D^{25}$ +14.8° (*c* 1.284, $CHCl_3$); Optical purity 96.9% ee.

Optical Resolution of 5b. (−)-(*S*)-1-Phenylethylamine (16.6 g, 137.2 mmol) was added to a solution of **5b** (33.9 g, 136.7 mmol) in 200 ml of acetone. The solution was allowed to stand overnight at 0 °C. The salt which precipitated was collected by filteration and subsequent further fractional crystallization was carried out. (yield 10.37 g; $[\alpha]_D^{25}$ −0.83° (*c* 1.014, CH_3OH); mp 128—131 °C). Subsequent liberation of the acid, extraction, and evaporation gave optically pure (+)-**5b** in 6.17 g (18.2%) yield: Mp 144—146 °C; $[\alpha]_D^{20}$ +9.25° (*c* 1.794, $CHCl_3$); Optical purity (96.5% ee) was determined by HPLC with Daicel Chiralcel OD-H eluted with 8 vol% 2-propanol in hexane; flow rate 0.5 ml min^{-1}; UV detector 215 nm; temperature 30 °C; retention time; 13.0 min for (−)-**5b**, 14.0 min for (+)-**5b**.

(+)-(*R*)-1-Phenylethylamine (16.8 g, 139.1 mmol) was added to a solution of **5b** (34.5 g, 139.1 mmol) in 100 ml of acetone. The solution was allowed to stand overnight at 0 °C. The salt which precipitated was collected by filteration and subsequent further fractional crystallization was carried out. (yield 14.1 g; $[\alpha]_D^{25}$ +3.42° (*c* 1.072, CH_3OH); mp 135—138 °C). Subsequent liberation of the acid, extraction, and evaporation gave optically pure (−)-**5b** in 6.08 g (17.7%) yield: Mp 148—150 °C; $[\alpha]_D^{20}$ −10.79° (*c* 1.112, $CHCl_3$); Optical purity 98.9% ee.

The Kolbe Coupling Reaction of (±)-5a. The phosphinoyl carboxylic acid (±)-**5a** (2.00 g, 8.52 mmol) and sodium methoxide (30 mg, 0.56 mmol) were dissolved in 30 ml of MeOH. The mixture was cooled with ice water, and the solution was electrolyzed at a constant current of 0.7 amp. (ca. 27—28 volt., current density 87.5 mA cm^{-2}) for 2 h. The reaction was monitored by measuring the conversion ratio of the starting acid by HPLC every 15 min. The colorless reaction mixture was then concentrated under reduced pressure. The resulting solid residue was dissolved in chloroform, and washed with water, and saturated $NaHCO_3$, and dried (Na_2SO_4). Removal of the solvent gave a crude solid (1.80 g),

which was chromatographed over silica gel (Wakogel C-200) using ethyl acetate-methanol mixtures gradually enriched in methanol; 20 ml portions of eluent were collected.

Fraction 1 (colorless oil, 0.12 g, 6.2%) was assigned as methyl [methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]acetate (**9a**): ^{1}H NMR ($CDCl_3$) δ = 1.07 (s, 9H), 1.34 (dd, 6H, ^3J = 17.8 Hz, J_{vic} = 4.2 Hz), 1.58 (d, 3H, ^2J = 11.9 Hz), 1.55 (dd, 2H, ^3J = 7.3 Hz, J_{vic} = 3.1 Hz), 2.81—3.03 (m, 2H), 3.76 (s, 3H); ^{31}P NMR ($CDCl_3$) δ = 54.33 (s); FAB-MS (Pos., *m/z*) 249 $[M+H]^+$.

Fraction 2 (colorless oil, 0.23 g, 12.8%) was assigned as methyl [methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]methyl ether (**10a**): ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 9H), 1.35 (d, 6H, ^3J = 16.6 Hz), 1.44 (d, 3H, ^2J = 11.9 Hz), 1.63 (m, 2H), 3.45 (s, 3H), 3.81 (m, 2H); ^{31}P NMR ($CDCl_3$) δ = 56.33 (s); FAB-MS (Pos., *m/z*) 221 $[M+H]^+$.

Fraction 3 (colorless crystal, 0.69 g, 38.6%) was assigned as *meso*-1,2-bis[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]ethane (*meso*-**6a**): Mp 199—200 °C; ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 18H), 1.32—1.41 (m, 18H), 1.47—1.61 (m, 4H), 1.83—2.02 (m, 4H); ^{13}C NMR ($CDCl_3$) δ = 8.47 (m), 16.50 (m), 21.44 (d, ^2J = 4.2 Hz), 32.12 (s), 33.37 (t, ^2J = 7.3 Hz), 36.74 (m), 46.05 (s); ^{31}P NMR ($CDCl_3$) δ = 58.49 (s); FT-IR (KBr) 1137 cm^{-1}; FAB-MS (Pos., *m/z*) 379 $[M+H]^+$.

Fraction 4 (colorless crystal, 0.58 g, 32.2%) was assigned as *dl*-1,2-bis[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]ethane (*dl*-**6a**): Mp 129—131 °C; ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 18H), 1.32—1.42 (m, 18H), 1.51—1.62 (m, 4H), 1.69—1.81 (m, 2H), 2.18—2.29 (m, 2H); ^{31}P NMR ($CDCl_3$) δ = 57.24 (s); FT-IR (KBr) 2954, 1687, 1479, 1157, 864 cm^{-1}; FAB-MS (Pos., *m/z*) 379 $[M+H]^+$.

The Kolbe Coupling Reaction of (−)-5a. The Kolbe coupling reaction of (−)-**5a** was carried out in a similar manner to that described above. The yield, melting point, optical rotation, NMR spectra, IR spectra and FAB-MS spectra were as follows: (−)-1,2-Bis[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]ethane ((−)-**6a**): Yield 61.0%; mp 117—119 °C; $[\alpha]_D^{26}$ −2.85° (*c* 1.05, $CHCl_3$);[12] ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 18H), 1.31—1.41 (m, 18H), 1.49—1.62 (m, 4H), 1.70—1.81 (m, 2H), 2.17—2.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 9.76 (m), 17.38 (m), 21.53 (d, ^2J = 4.9 Hz), 32.12 (s), 33.37 (t, ^2J = 7.0 Hz), 37.09 (m), 45.97 (s); ^{31}P NMR ($CDCl_3$) δ = 57.39 (s); FT-IR (KBr) 2954, 1480, 1158, 863 cm^{-1}; FAB-MS(Pos., *m/z*) 379 $[M+H]^+$. Anal. Calcd for $C_{20}H_{44}O_2P_2$: C, 63.46; H, 11.72%. Found: C, 63.75; H, 11.85%.

The Kolbe Coupling Reaction of (+)-5a. The Kolbe coupling reaction of (+)-**5a** was carried out in a similar manner to that described above. The yield, melting point, optical rotation, NMR spectra, IR spectra and FAB-MS spectra were as follows: (+)-1,2-bis[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]ethane ((+)-**6a**): Yield 59.0%; mp 123—126 °C; $[\alpha]_D^{26}$ +2.36° (*c* 0.846, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 18H), 1.31—1.41 (m, 18H), 1.48—1.59 (m, 4H), 1.69—1.81 (m, 2H), 2.18—2.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ = 9.66 (m), 17.28 (m), 21.46 (d, ^2J = 4.9 Hz), 32.07 (s), 33.31 (t, ^2J = 7.3 Hz), 37.04 (m), 45.93 (s); ^{31}P NMR ($CDCl_3$) δ = 57.71 (s); FT-IR (KBr) 2954, 1480, 1158, 863 cm^{-1}; FAB-MS(Pos., *m/z*) 379 $[M+H]^+$.

The Kolbe Coupling Reaction of (±)-5b. The Kolbe coupling reaction of (±)-**5b** was carried out in a similar manner to that described above. Chromatography on silica gel gave six portions.

Fraction 1 (colorless oil, 3.7%) was assigned as methyl(1,1,3,3-tetramethylbutyl)vinylphosphine oxide (**11**): ^{1}H NMR ($CDCl_3$) δ = 1.05 (s, 9H), 1.31 (dd, 6H, ^3J = 16.3 Hz, J_{vic} = 2.4 Hz), 1.45 (d, 3H, ^2J = 11.2 Hz), 1.56 (d, 2H, ^3J = 4.8 Hz), 6.15—6.34 (m, 3H); ^{31}P NMR ($CDCl_3$) δ = 46.95 (s); FT-IR (neat) 2954, 1474, 1390, 1366, 1180, 989, 882 cm^{-1}; GC-MS (Pos., *m/z*) 202 $[M]^+$.

Fraction 2 (colorless oil, 9.3%) was assigned as methyl 3-[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]propionate (**9b**): ^{1}H NMR ($CDCl_3$) δ = 1.07 (s, 9H), 1.33 (d, 6H, ^3J = 17.1 Hz), 1.39 (d, 3H, ^2J = 11.1 Hz), 1.54 (dd, 2H, ^3J = 7.8 Hz, J_{vic} = 1.5 Hz), 1.86—1.97 (m, 1H), 2.05—2.17 (m, 1H), 2.57—2.80 (m, 2H), 3.71 (s); ^{31}P NMR ($CDCl_3$) δ = 57.13 (s); FAB-MS (Pos., *m/z*) 263 $[M+H]^+$.

Fraction 3 (colorless oil, 2.5%) was assigned as ethylmethyl-(1,1,3,3-tetramethylbutyl)phosphine oxide (**12**): ^{31}P NMR ($CDCl_3$) δ = 56.89 (s); FAB-MS (Pos., *m/z*) 205 $[M+H]^+$.

Fraction 4 (colorless oil, 9.1%) was assigned as methyl 2-[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]ethyl ether (**10b**): ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 9H), 1.32 (d, 6H, ^3J = 16.8 Hz), 1.37—1.54 (m, 5H), 1.73—1.96 (m, 2H), 3.44 (s, 3H), 3.69—3.80 (m, 2H); ^{31}P NMR ($CDCl_3$) δ = 60.68 (s); FAB-MS (Pos., *m/z*) 235 $[M+H]^+$.

Fraction 5 (colorless crystal, 35.2%) was assigned as *meso*-1,4-bis[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]butane (*meso*-**6b**): Mp 160—161 °C; ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 18H), 1.31 (dd, 12H, ^3J = 16.5 Hz, J_{vic} = 1,2 Hz), 1.34 (d, 6H, ^2J = 11.1 Hz), 1.52 (dd, 4H, ^3J = 8.3 Hz, J_{vic} = 1.2 Hz), 1.49—1.87 (m, 8H); ^{13}C NMR ($CDCl_3$) δ = 8.77 (d, ^1J = 61.9 Hz), 21.43 (d, ^2J = 6.8 Hz), 23.79 (m), 24.28 (d, ^1J = 61.9 Hz), 32.09 (s), 33.27 (d, ^2J = 13.6 Hz), 36.45 (d, ^1J = 66.4 Hz), 45.99 (s); ^{31}P NMR ($CDCl_3$) δ = 57.35 (s); FT-IR (KBr) 2952, 2912, 1674, 1473, 1120, 843 cm^{-1}; FAB-MS (Pos., *m/z*) 407 $[M+H]^+$.

Fraction 6 (colorless crystal, 27.1%) was assigned as *dl*-1,4-bis-[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]butane (*dl*-**6b**): Mp 81—83 °C; ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 18H), 1.31 (dd, 12H, ^3J = 16.7 Hz, J_{vic} = 1.5 Hz), 1.35 (d, 6H, ^2J = 10.8 Hz), 1.52 (dd, 4H, ^3J = 8.2 Hz, J_{vic} = 1.1 Hz), 1.47—1.86 (m, 8H); ^{31}P NMR ($CDCl_3$) δ = 57.93 (s); FT-IR (KBr) 2950, 2915, 1642, 1469, 1135, 871 cm^{-1}; FAB-MS (Pos., *m/z*) 407 $[M+H]^+$.

The Kolbe Coupling Reaction of (−)-5b. The Kolbe coupling reaction of (−)-**5b** was carried out in a similar manner to that described above. The yield, melting point, optical rotation, NMR spectra, IR spectra and FAB-MS spectra were as follows: (−)-1,4-Bis[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]butane ((−)-**6b**): Yield 64.5%; mp 98—99 °C; $[\alpha]_D^{22}$ −2.61° (*c* 1.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 1.07 (s, 18H), 1.31 (d, 12H, ^3J = 18.3 Hz), 1.37 (d, 6H, ^2J = 11.1 Hz), 1.52 (d, 4H, ^2J = 8.1 Hz), 1.47—1.86 (m, 8H); ^{31}P NMR ($CDCl_3$) δ = 58.08 (s); FT-IR (KBr) 2951, 2910, 1639, 1468, 1136, 876 cm^{-1}; FAB-MS(Pos., *m/z*) 407 $[M+H]^+$; Anal. Calcd for $C_{22}H_{48}O_2P_2$: C, 64.99; H, 11.90%. Found: C, 65.23; H, 12.11%.

The Kolbe Coupling Reaction of (+)-5b. The Kolbe coupling reaction of (+)-**5b** was carried out in a similar manner to that described above. The yield, melting point, optical rotation, NMR spectra, IR spectra and FAB-MS spectra were as follows: (+)-1,4-Bis[methyl(1,1,3,3-tetramethylbutyl)phosphinoyl]butane ((+)-**6b**): Yield 60.2%; Mp 99—101 °C; $[\alpha]_D^{22}$ +2.72° (*c* 0.986, $CHCl_3$); ^{1}H NMR ($CDCl_3$) δ = 1.06 (s, 18H), 1.32 (d, 12H, ^3J = 16.7 Hz), 1.36 (d, ^2J = 11.4 Hz), 1.52 (d, ^3J = 8.1 Hz, 4H), 1.47—1.83 (m, 8H); ^{31}P NMR ($CDCl_3$) δ = 57.53 (s); FT-IR (KBr) 2949, 2911, 1635, 1467, 1134, 880 cm^{-1}; FAB-MS(Pos., *m/z*) 407 $[M+H]^+$.

Oxidative Decarboxylation of (−)-5b. In a 300 ml four-neck flask, (−)-**5b** (5.03 g, 20.3 mmol), anhydrous copper(II) acetate (0.65 g, 3.6 mmol), pyridine (0.13 g, 1.5 mmol), and 30 ml of chlorobenzene were added at room temperature and stirred for 0.5 h. Then lead(IV) acetate (8.9 g, 20.1 mmol) was added under nitrogen atmosphere and stirred in dark place for 1 h. The mixture was heated at 80 °C for 8 h. The solvent was removed by an evaporator. The resulting product was dissolved in 300 ml of chlo-

roform, and washed with 300 ml of water, dried (Na_2SO_4), and concentrated. The green residue (4.85 g) was subjected to simple distillation under reduced pressure. Thus, 1.20 g (yield 25.0%) of (+)-methyl(1,1,3,3-tetramethylbutyl)vinylphosphine oxide ((+)-**11**) could be isolated: Bp 109—112 °C/16 mmHg; $[\alpha]_D^{24}$ +29.15° (*c* 1.86, $CHCl_3$); Optical purity (98.0% ee) was determined by HPLC with Daicel Chiralcel OD-RH (CH_3CN : H_2O = 4 : 1; flow rate 0.5 ml min^{-1}; UV detector 215 nm; temperature 30 °C; retention time; 16.7 min for (+)-**11**, 18.5 min for (+)-**11**; ^1H NMR ($CDCl_3$) δ = 1.05 (s, 9H), 1.31 (dd, 6H, ^3J = 16.3 Hz, J_{vic} = 2.4 Hz), 1.45 (d, 3H, ^2J = 11.2 Hz), 1.56 (d, 2H, ^3J = 4.8 Hz), 6.15—6.34 (m, 3H); ^{31}P NMR ($CDCl_3$) δ = 46.95 (s); FT-IR (neat) 2954, 1474, 1390, 1366, 1180, 989, 882 cm^{-1}; GC-MS (Pos., *m/z*) 202 $[M]^+$.

Oxidative Decarboxylation of (+)-5b. Oxidative decarboxylation of (+)-**5b** was carried out in a similar manner to that described above. The yield and optical rotation were as follows: (−)-methyl(1,1,3,3-tetramethylbutyl)vinylphosphine oxide ((−)-**11**): Yield 32.6%; $[\alpha]_D^{23}$ −30.07° (*c* 0.789, $CHCl_3$); Optical purity 99.0% ee.

Free-Radical Addition of Secondary Phosphine to (+)-11. In a 50 ml two-neck flask, (+)-**11** (0.92 g, 4.55 mmol), **3** (0.73 g, 4.55 mol), and *t*-butyl peroxy-2-ethylhexanoate (0.09 g, 0.42 mmol) were mixed. The mixture was heated at 130 °C for 6 h under nitrogen. The resulting product was dissolved in 100 ml of chloroform and 34% hydrogen peroxide (0.50 g, 5.0 mmol) was added at room temperature. The mixture was kept at 60 °C for 1 h. The mixture was washed with 100 ml of NaOH solution, dried (Na_2SO_4), and concentrated. The colorless residue (1.60 g) was chromatographed in exactly the same manner as described for the Kolbe coupling reaction of **5a**. The yield, melting point, and optical rotation were as follows. (*meso*-**6a**): Yield 40.1%; mp 197—199 °C: ((+)-**2a**); yield 39.2%; mp 123—127 °C; $[\alpha]_D^{20}$ +2.80° (*c* 1.24, $CHCl_3$).

Preparation of Bisphosphine–Borane (8a). In a 10 ml flask, (+)-**6a** (160 mg, 0.42 mmol) and phenylsilane 3.67 g (33.9 mmol) were mixed under nitrogen. The mixture was heated at 110 °C for 12 h. Any remaining phenylsilane was removed under reduced pressure to leave a pasty oil. To this, a solution of KOH (560 mg, 10 mmol) in 3 ml of degassed EtOH–H_2O (10 : 1) was added with stirring. The solution was extracted three times by 5 ml of degassed Et_2O. The combined extracts were dried over Na_2SO_4, and evaporated under reduced pressure to leave 135 mg of bisphosphine (**7a**). Yield about 92%; ^{31}P NMR ($CDCl_3$) δ = −4.53 (s).

To a stirred, cooled solution of **7a** (130 mg, 0.38 mmol) in dry THF (5 ml) was slowly added THF–BH_3 (1/1) complex (1 ml of 1.0 M THF solution, 1.0 mmol) under nitrogen. After 1 h stirring, the solvent was evaporated under reduced pressure to leave a crude solid (155 mg). Recrystallization from hot toluene afforded (−)-**8a** as colorless needles (95 mg, 66.8%); mp 148—149 °C; $[\alpha]_D^{20}$ −5.56° (*c* 0.53, $CHCl_3$); ^1H NMR ($CDCl_3$) δ = 0.59 (br q, 6H, *J* = 114.6 Hz), 1.05 (s, 18H), 1.20 (d, 6H, ^2J = 9.2 Hz), 1.32 (d, 12H, ^3J = 16.1 Hz), 1.52 (d, 4H, ^3J = 7.5 Hz), 1.52—1.64 (m, 2H), 1.92—2.07 (m, 2H); ^{31}P NMR ($CDCl_3$) δ = 34.97 (s); FT-IR (KBr) 2958, 2379, 1370, 1475, 1064, 761 cm^{-1}; FAB-MS (Pos., *m/z*) 375 $[M+H]^+$.

Preparation of (*S*,*S*)-1,2-Bis(P-boratemethyl(1,1,3,3-tetramethylbutyl)phosphino)ethane (*S*,*S*)-*t*-Octyl-BisP*–Borane.[6] In a 500 ml four-neck flask, **1** (52.8 g, 0.347 mol), iodomethane (55.1 g, 0.38 mol) and 200 ml of methanol was added at room temperature and refluxed for 9 h. The excess iodomethane and solvent were removed by an evaporator. The resulting solid was dissolved in 300 ml of 5 M NaOH solution under nitrogen atmosphere, and extracted with 300 ml of hexane. The extracts were washed with water, dried (Na_2SO_4), and concentrated. The residue was subjected to simple distillation at reduced pressure. Thus, 49.1 g (81.4%) of dimethyl(1,1,3,3-tetramethylbutyl)phosphine could be isolated: Bp 48—49 °C/0.4—0.5 mmHg; ^1H NMR ($CDCl_3$) δ = 0.90 (d, 6H, ^2J = 2.76 Hz), 1.03 (s, 9H), 1.11 (d, 6H, ^3J = 12.29 Hz), 1.35 (d, 2H, ^3J = 8.44 Hz); ^{13}C NMR ($CDCl_3$) δ = 8.76 (d, ^1J = 18.86 Hz), 24.16 (d, ^2J = 11.54 Hz), 30.57 (d, ^4J = 10.94 Hz), 32.09 (s), 33.12 (d, ^3J = 9.13 Hz), 51.00 (d, ^2J = 15.24 Hz); ^{31}P NMR ($CDCl_3$) δ = −20.88 (s); GC-MS (*m/z*) 174 (M^+).

To a stirred, cooled solution of dimethyl(1,1,3,3-tetramethylbutyl)phosphine (13.7 g, 75.6 mol) in dry THF (150 ml) was slowly added THF–BH_3 (1/1) complex (77 ml of 1.0 M THF solution, 77 mol) under nitrogen. After 3 h stirring, the solvent was evaporated under reduced pressure to leave a crude solid (13.8 g). Recrystallization from hot ethyl acetate afforded dimethyl(1,1,3,3-tetramethylbutyl)phosphine–borane (1/1) as colorless needles (11.2 g, 78.7%): Mp 39—40 °C; ^1H NMR ($CDCl_3$) δ = 0.43 (br q, J_{HB} = 101.9 Hz, 3H), 1.05 (s, 9H), 1.42 (d, ^2J = 9.70 Hz, 6H), 1.29 (d, ^3J = 15.95 Hz, 6H), 1.50 (d, ^3J = 7.90 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ = 6.97 (dq, *J* = 129.1 Hz, *J* = 34.78 Hz), 21.89 (dq, *J* = 126.6 Hz, *J* = 4.98 Hz), 30.67 (s), 31.90 (tq, *J* = 123.4 Hz, *J* = 4.64 Hz), 33.03 (d, *J* = 8.68 Hz), 46.50 (t, *J* = 121.3 Hz); ^{31}P NMR ($CDCl_3$) δ = 26.68 (d, *J* = 65.6 Hz); FAB-MS (Pos., *m/z*) 189 $[M+H]^+$.

To a stirred, cooled (−78 °C) solution of (−)-sparteine (11.29 g, 48.2 mmol) in dry Et_2O (100 ml) was added *s*-BuLi (48 ml of 1.0 M cyclohexane and *hexane* solution, 48 mmol) under nitrogen. After 1 h, a solution of dimethyl(1,1,3,3-tetramethylbutyl) phosphine–borane (1/1) (7.71 g, 41 mmol) in dry Et_2O (40 ml) was added dropwise, and the mixture was stirred at −78 °C. Three hours later, dry $CuCl_2$ (8.00 g, 59.5 mmol) was added in one portion with vigorous stirring, and the mixture was gradually warmed to room temperature in 2 h. After stirring for an additional 1 h, the reaction solution was quenched by the addition of 25% aqueous ammonia (60 ml). The organic layer was separated and the aqueous layer was extracted with 200 ml of ethyl acetate for two times. The combined organic layer was washed with 5% NH_4OH, 2 M HCl, and brine, and then dried over Na_2SO_4. The solvent was removed on an evaporator to leave a white residue, which was recrystallized from hot toluene to give pure (−)-(*S*,*S*)-*t*-Octyl-BisP*–borane (1/2) as colorless needles. (Yield 34.5%); mp 149—151 °C; $[\alpha]_D^{20}$ −5.68° (*c* 0.965, $CHCl_3$).

Preparation of Rhodium Complex (9a). A solution of (*S*,*S*)-**7a** (0.13 g, 0.38 mmol) in 5 ml of dry THF was added to a suspension of $[Rh(nbd)_2]BF_4$ (0.13 g, 0.35 mmol) in 10 ml of THF under nitrogen. The mixture turned to a clear solution instantly; this was filtered to remove a small amount of precipitates. The filtrate was evaporated under reduced pressure and any residual oil was washed with hexane to give orange powder (195.3 mg, yield; 88.8 %).

Asymmetric Hydrogenation (Run 2). In a 50 ml glass autoclave, methyl 2-acetamidoacrylate (143.4 mg, 1.0 mmol) and **9a** (1.3 mg, 0.002 mmol) were charged under nitrogen. The vessel was evacuated and filled hydrogen to a pressure of 2 atm. Five ml of anhydrous, degassed methanol was added quickly at 0 °C. After four vacuum/H_2 cycles, the vessel was pressurized to an initial pressure of 2 atm. The solution was stirred at room temperature until no further uptake was observed. The resulting solution was submitted to direct analysis for the ee value by GC. Enantiomeric excess (96.3% ee) was determined by Capillary GC with Chrompack's Chiral-L-Val column (25mL; 120 °C isothermal; carrier gas He; flow rate 1.48 ml min^{-1}; FID detector), retention time: 6.45 min for (*R*)-*N*-acetylalanine methyl ester, 7.09 min for (*S*)-*N*-acetylalanine methyl ester.

Asymmetric Hydrogenation (Run 6). Asymmetric hydrogenation of α-acetamidocinnamic acid (205.2 mg, 1.0 mmol) was carried out in a similar manner to that described above. Reaction solution was converted to the corresponding methyl ester by the reaction with trimethylsilyldiazomethane. Enantiomeric excess (93.5% ee) was determined by HPLC with Daicel Chiralcel OD-H 10% 2-PrOH/hexane; flow rate 1.0 ml min^{-1}; UV detector 215 nm; temperature 30 °C; retention time; 9.07 min for (*R*)-*N*-acetylphenylalanine methyl ester, 11.37 min for (*S*)-*N*-acetylphenylalanine methyl ester.

Conclusion

In conclusion, we report a new approach to P-chiral bisphosphine ligands (BisP*) and related bisphosphines based on the electrochemical Kolbe coupling of chiral phosphinoyl carboxylic acids. BisP* having a new bulky alkyl group (*t*-octyl or 1,1,3,3-tetramethylbutyl), 1,2-bis[methyl(1,1,3,3-tetramethylbutyl)phosphino]ethane, was synthesized. Asymmetric hydrogenation of α-(acylamino)acrylic acids by a rhodium complex with this ligand affords *N*-acylamino acids in 94—96% ee.

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